U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-282 232

Paraquat Sorption as a Function of Particle Size in Natural Sediments

Environmental Research Lab, Athens, Ga

6 Jun 77

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/J-78-013	2. JOURNAL ARTICLE	3. RE PB 282 232
4. TITLE AND SUBTITLE: Paraquat Sorption as a Function of Particle Size in Natural Sediments		5. REPORT DATE
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): Samuel W. Karickhoff and David S. Brown		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Environmental Research Laboratory, U.S. Environmental Protection Agency, College Station Road, Athens, GA 30605		10. PROGRAM ELEMENT NO. 1BB770
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS: U.S. Environmental Protection Agency -Athens, GA, Environmental Research Laboratory, College Station Road, Athens, GA 30605		13. TYPE OF REPORT AND PERIOD COVERED Journal Article
		14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES
Published in Journal of Environmental Quality, 7 (2): 246-252 (April - June 1978). Contact: S.W. Karickhoff, 8-250-3593

16. ABSTRACT

The distribution of sorbed paraquat (1,1' -dimethyl-4,4'-bypyiridinium ion) as a function of particle size (sand through clay) was determined on five natural sediments. Paraquat concentrations in individual size fractions varied as much as two orders of magnitude within a given sediment, showing a pronounced preference for the fine silt and clay fractions. Adsorption isotherms were measured for individual size separates on one sediment. Paraquat distributions in the whole sediment agreed well with those computed using the isotherm coefficients determined on individual size separates. Paraquat sorbs by ion exchange, and sorption partition coefficients showed a definite correlation with the cation exchange capacity (CEC) of individual size fractions. However, exchange sites in different fractions differed in their effectiveness in sorbing paraquat, with the fine silt and clay exchange sites being more effective than those of the larger separates.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Sorption Adsorption Cation exchanging Sediments Clay minerals	Paraquat Hectorite	06 F 13 B

18. DISTRIBUTION STATEMENT: Release to Public	REPRODUCED BY NATIONAL TECHNICAL INFORMATION SERVICE U.S. DEPARTMENT OF COMMERCE SPRINGFIELD, VA. 22161	21. NO. OF PAGES 10
	S (This page) d	22. PRICE A02 - A01

EPA Form 2220-1 (9-73)

EPA-600/J-78-013
JOURNAL ARTICLE

Reprinted from the *Journal of Environmental Quality*
Vol. 7, no. 2, April-June 1978. Copyright © 1978, ASA, CSSA, SSSA
677 South Segoe Rd., Madison, WI 53711 USA

Paraquat Sorption as a Function of Particle Size in Natural Sediments

SAMUEL W. KARICKHOFF AND DAVID S. BROWN

Paraquat Sorption as a Function of Particle Size in Natural Sediments[1]

SAMUEL W. KARICKHOFF AND DAVID S. BROWN[2]

ABSTRACT

The distribution of sorbed paraquat (1,1'-dimethyl-4,4'-bypyiridinium ion) as a function of particle size (sand through clay) was determined on five natural sediments. Paraquat concentrations in individual size fractions varied as much as two orders of magnitude within a given sediment, showing a pronounced preference for the fine silt and clay fractions. Adsorption isotherms were measured for individual size separates on one sediment. Paraquat distributions in the whole sediment agreed well with those computed using the isotherm coefficients determined on individual size separates. Paraquat sorbs by ion exchange, and sorption partition coefficients showed a definite correlation with the cation exchange capacity (CEC) of individual size fractions. However, exchange sites in different fractions differed in their effectiveness in sorbing paraquat, with the fine silt and clay exchange sites being more effective than those of the larger separates.

In pure clay suspensions (hectorite and montmorillonite), sorbed paraquat did not distribute uniformly throughout the clay particle size range. The concentration peaked in the mid-size range (0.065–0.44 μm, equivalent Stokes radii) and decreased uniformly in the larger and smaller particle sizes. Peak concentrations were two to five times those of the less sorbing components. Because no corresponding trend was found in NH_4^+-measured CEC's, exchange sites in the median clay particle size ranges seemed to be more "effective" in sorbing paraquat than the extreme size ranges.

UV spectra of paraquat in a hectorite suspension revealed that, after 4 hours of centrifuging at 20,000 rpm, >50% of the paraquat remaining in the suspended (water) phase was sorbed on particulates not removed by centrifugation. Therefore, for highly sorbed compounds such as paraquat, conventional phase separation techniques for measuring sorption may not distinguish sorbed vs. "free" compounds.

Additional Index Words: **hectorite, cation exchange, adsorption isotherms, particle-size fractionation, phase separation.**

Pesticides may enter watercourses in the sorbed form (bound on sediment carriers) or become sorbed subsequent to entry into the water. In the short term, therefore, sorption processes may constitute a removal mechanism resulting in the gradual accumulation of concentrated residues available for release later. As accumulators, the available sediment surfaces may act either as sources or sinks for potentially toxic pollutants, depending on prevailing conditions.

Sorption to natural sediments involves: (i) adsorption or physical bonding of adsorbates in an interfacial re-

[1] Contributed from work done at the Environ. Res. Lab., USEPA, Athens, GA 30605. Received 6 June 1977.

[2] Research Chemist and Research Soil Scientist, respectively.

gion between the sediment and aqueous phases, (ii) absorption of the sorbates into sediment components, or (iii) chemical bonding of the sorbates to sediment components. The degree to which sorption processes influence the behavior of organic-water-sediment systems depends on (i) the relative amounts of sediment and water in the system, (ii) the degree of preference the sorbate shows for the sediment relative to the bulk solution, and (iii) the degree of change in the chemical behavior of the sorbate resulting from the sorption process.

Natural sediments are commonly classified according to particle size, organic and mineralogical composition, cation exchange capacity, and surface area. Particle size greatly influences transport phenomena as well as sorption processes. Several recent predictive modeling approaches (2, 6, 11) have recognized the need to separate total sediment loads into several size fractions to better simulate transport of sediments and sorbed pollutants in the environment. These efforts place new emphasis on the importance of pollutant distributions as a function of particle size in predicting pollutant transport. The distribution of compounds that show strong particle size partitioning preferences may be a key factor in determining exposure levels for some aquatic organisms. Organisms whose primary habitats are the most heavily pollutant-laden sediment fractions would be influenced by much higher pollutant concentrations than would be indicated by an overall average of pollutant load. This work investigates the sorption characteristics of an organic cation as a function of particle size in a broad spectrum of natural sediments.

MATERIALS AND METHODS

PARTICLE SIZE FRACTIONATION

Selected for study were five bottom sediments (Table 1) that provide a range of inorganic and organic compositional differences; no effort was made to collect samples that would be representative of any given water source or geographical region. Particle size fractionation procedures used in the study were similar to those outlined by Jackson (5) except that no dispersants or other additives were used. Sands were separated by wet sieving, silts by sedimentation, and clay by timed centrifugation using a Sorvall RC2-B centrifuge with a SS-34 rotor. All the sand and silt separates were washed five times and the two larger clay fractions were washed once. To maintain sample volumes at a manageable level, only the first two sand and silt washes were recombined for further separation. The particle size breakouts were: sand (>64 μm), coarse silt (64–20 μm), medium silt (20–5 μm), fine silt (5–2 μm), coarse clay (2–0.2 μm), medium clay (0.2–0.08 μm), fine clay (<0.08 μm). Carbon analyses were run by Galbraith Laboratories, Inc.,[1] Knoxville, Tenn. Cation exchange capacities (CEC) were determined by the standard ammonium ion saturation and steam distillation method. Clay fractions were saturated using an ammonium-saturated Rexyn AG-50 column; sand and silt separates were saturated by repeated washings with 1*N* NH_4Cl and distilled water rinses.

Table 1—Natural bottom sediments

Sample location	General character
Georgia I—composite of numerous samples taken over approximately 1.6 km (1 mi) of small stream	Largely sand; fine material forms stable red-brown suspension
Georgia II—single sample taken at onset of continuous flow of small stream	Same as Georgia I
Santa Maria River, Ariz.—single sample, low flow river	Nearly all coarse to fine sand, very little suspendable material
Macon Bayou, Tallalah, La.—single sample	Large amount of silt and clay, very low sand
Weatherford Lake, Fort Worth, Tex.—single sample	Medium sand; large amount of brown-black suspendable material

ADSORPTION ISOTHERMS

Adsorption isotherms were run on the sand, the three silt fractions, and the combined clay fraction (<2 μm) of the Georgia I stream sediment. Constant amounts of each sediment fraction were combined with variable concentrations of paraquat (1,1′-dimethyl-4,4′-bypyiridinium ion). Paraquat levels at the low concentration end of the isotherm were chosen to give equilibrium solution concentrations less than or equal to the analytical detection limit (50 ppb). At the high end, paraquat concentrations were in excess of the amount required to saturate the sediment. Dependence of the isotherm on sediment concentrations was tested by running two concentrations each of the sand and clay fractions (Table 2). Sands and silts were weighed out in air-dry condition. Clays were pipetted from suspensions of known concentration, as determined by drying aliquots at 100°C for 24 hours. Paraquat-sediment suspensions were shaken vigorously for 15 min, allowed to stand for 1 hour, and phase-separated by a centrifugation step sufficient to remove particulates having equivalent Stokes' radii >0.02 μm. Paraquat analyses were run on water phase aliquots taken from the upper portion of the centrifuge tube. All samples were run in duplicate, and the mean values reported. Mass balance was checked periodically.

PARAQUAT DISTRIBUTION IN NATURAL SEDIMENTS

Paraquat, as the dichloride salt, was added to the five natural sediments (Table 1), stirred vigorously for 1 hour, and allowed to stand for at least 2 days. All sediment samples were weighed wet and those with high and low sand contents were made up to approximate concentrations of 1.0 and 0.5 kg sediment, respectively, in 4 liters of

[1] Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the USEPA.

Table 2—Isotherm coefficients for Georgia I sediment

Sediment fraction†	Sediment conc.	K_p'	Midpoint of K_p range	X_c	CEC	CEC	Avg. coefficient of variation‡
	mg/ml			ppm		meq/100 g	
Sand	200	300–500	400	380	600	0.47	0.33
Sand	100	300–750	530	390	600	0.47	0.39
C. silt	20	20,000–30,000	25,000	5,900	6,000	4.7	0.15
M. silt	10	30,000–40,000	35,000	7,500	7,800	6.17	0.09
F. silt	5	150,000–350,000	250,000	10,000	9,300	7.35	0.08
Clay	1	500,000–1,000,000	750,000	17,000	22,000	17.39	0.21
Clay	0.1	500,000–1,000,000	750,000	21,000	22,000	17.39	0.17

† C = coarse, M = medium, F = fine.

‡ A coefficient of variation (ratio of standard deviation to the mean) was determined on the measured water concentrations for each set of replicated samples generating a single plotted isotherm point; the number indicated above is an average over all isotherm points.

water. Paraquat additions were made so that the overall concentrations relative to the wet weight of the sediments were approximately 25 ppm. Resulting suspensions were separated into several particle-size fractions and each fraction was analzyed for paraquat. In all samples, paraquat levels in the liquid phase were below the limit of detection.

In natural sediments and waters, paraquat was analyzed colorimetrically by the Chevron method as modified by Pope and Benner (10). Spectra were run on a Perkin Elmer 356 Spectrophotometer with absorbance ranges of 1.0 to 0.03 and pathlengths of 1.0 to 10.0 cm, giving an overall detection limit for paraquat in water of 50 ppb. Minor modifications were made in Pope and Benner's sediment analysis procedure relative to digestion and sample size. All samples were digested in 18*N* H_2SO_4 for 12 hours. Sample sizes and acid volumes varied for the different size fractions depending on detection limits, paraquat concentrations, and the amount of sample available. Detection limits determined in the Georgia I sediment were 0.5 ppm for sand and approximately 2 ppm for silts and clays. Paraquat recoveries for this sediment were in excess of 75% for all fractions. Recoveries were not determined in isolated fractions of the nonlocal sediments. Total recoveries are given in Table 3. Replicate analyses on randomly selected natural sediment fractions showed the clay and silt paraquat determinations to vary < 10% of the mean value, whereas replicate sand determinations varied as much as a factor of two because of the difficulty in getting a representative sand sample and because of the low levels of paraquat (< 1 ppm) in many of the sand samples.

PARAQUAT-CLAY SYSTEMS

The < 2 μm fraction of clay minerals obtained from Wards Scientific Establishment were separated by sedimentation and percolated through a Rexyn Ag-50 exchange column saturated with the desired cation. Paraquat-clay suspensions were formed by mixing aliquots of paraquat solution and clay suspension drop-wise. Spectroscopic blanks were prepared for all samples by substituting water for paraquat in the same preparation. Paraquat concentrations were monitored by UV light absorption in situ in the clay suspensions using blank clay suspensions to cancel light absorption and scattering caused by the clay matrix. A standard curve was derived by preparing known concentrations (relative to suspension volume) of paraquat in hectorite suspensions. Paraquat concentrations in all the clay suspensions were maintained below the level (20% of the CEC) that would have flocculated the clay and prohibited blank cancellation in the quantification step.

RESULTS AND DISCUSSION

ADSORPTION ISOTHERMS ON A NATURAL SEDIMENT

Isotherms for the sand, silt, and clay fractions of the Georgia I sediment are shown in Fig. 1. These isotherms were fitted to the hyperbolic, Langmuir equation:

$$X = X_c K_p C/(X_c + K_p C) \qquad [1]$$

where X denotes the concentration of sorbate (paraquat) on the sediment relative to dry weight (ppm); C is the equilibrium solution sorbate concentration (ppm); K_p is the partition coefficient; and X_c is the adsorption capacity of sediment for paraquat.

The adsorption data were computer-fitted to Eq. [1] using MLAB (7), a digital computer program developed at NIH specifically for laboratory data applications. Table 2 gives the values of K_p and X_c derived from MLAB for the various particle-size fractions of the Georgia (I) stream sediment. Table 2 also gives the CEC for ammonium ion converted to paraquat concentration; this conversion assumed a one for two substitution of paraquat for ammonium ions. These CEC values correspond well with the X_c isotherm values, suggesting

Table 3—Paraquat distribution in natural sediments

Size fraction†	Total fraction mass	Total paraquat	Sediment paraquat conc.	Paraquat as % of CEC
	g	mg	ppm	
Georgia local stream I				
Sand	833.0	0.8	1	0.26
C. silt	44.9	0.9	21	0.35
M. silt	32.7	1.7	52	0.69
F. silt	14.0	4.6	330	3.3
C. clay	13.6	13.6	1,000	4.6‡
M. clay	0.53	0.4	760	–
F. clay	0.40	0.06	150	–
% paraquat recovered = 90%		$\bar{X}$ = 24 ppm (recovered)		
Georgia local stream II				
Sand	1,105.0	2.2	2	0.52
C. silt	14.3	0.5	36	0.61
M. silt	16.7	1.4	83	1.1
F. silt	8.8	4.8	550	5.5
C. clay	13.4	11.1	830	4.0‡
M. clay	0.63	0.5	760	–
F. clay	0.18	0.1	620	–
% paraquat recovered = 82%		$\bar{X}$ = 18 ppm (recovered)		
Santa Maria River				
Sand	1,095.0	2.2	2	0.87
C. silt	6.4	1.0	160	3.3
M. silt	2.8	2.6	920	9.0
F. silt	1.9	4.4	2,300	10.0
C. clay	1.6	9.6	6,000	9.2‡
M. clay	0.009	0.04	4,500	–
F. clay	0.006	0.01	2,300	–
% paraquat recovered = 79%		$\bar{X}$ = 18 ppm (recovered)		
Macon Bayou				
Sand	15.7	0.08	5	0.011
C. silt	58.5	0.1	2	0.018
M. silt	105.0	0.3	3	0.020
F. silt	28.0	0.3	9	0.041
C. clay	136.0	9.2	68	0.099‡
M. clay	20.1	3.6	180	–
F. clay	0.16	0.03	190	–
% paraquat recovered = 54%		$\bar{X}$ = 36 ppm (recovered)		
Weatherford Lake				
Sand	313.0	0.3	1	0.16
C. silt	51.2	0.4	7	1.8
M. silt	34.3	2.4	70	1.2
F. silt	8.2	0.8	92	2.4
C. clay	5.7	1.5	270	2.1
M. clay	0.3	0.2	540	–
F. clay	–	–	–	–
% paraquat recovered = 54%		$\bar{X}$ = 13 ppm (recovered)		

† C = coarse, M = medium, F = fine.

‡ This represents the combined clay fraction since limited sample size prohibited the determination of CEC on the subdivided clay separates.

paraquat is adsorbed primarily by a cation exchange mechanism on all the size fractions of the Georgia I sediment. Neither K_p nor X_c showed dependencies on sand concentration (Table 2). Both of these parameters, however, could be reduced as much as 30% by additional washing of the sand during fractionation. In the clay fractions, no dependence of K_p on clay concentration was observed, but X_c decreased as clay concentration increased. Some clay flocculation, which occurred prior to complete saturation with paraquat, resulted in partial site blockage and a reduction of the effective saturation capacity. The flocculation tendency increased with increasing clay concentration.

Paraquat adsorption isotherms for a variety of ad-

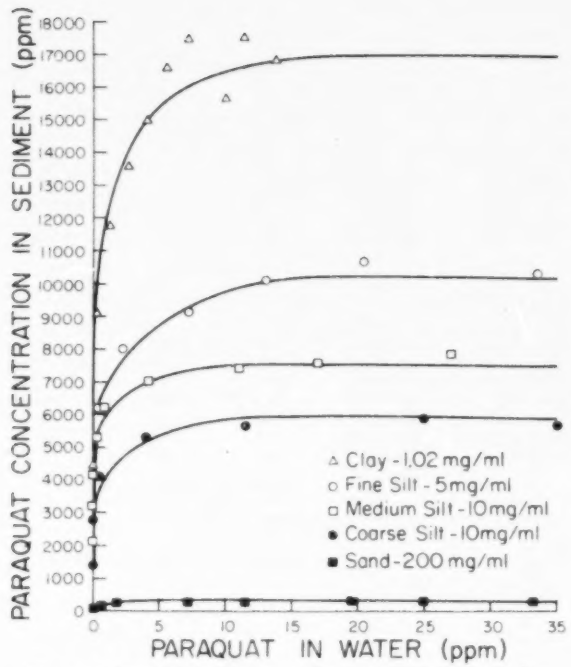
PARAQUAT CONCENTRATION IN SEDIMENT (ppm)
PARAQUAT IN WATER (ppm)
△ Clay - 1.02 mg/ml
○ Fine Silt - 5mg/ml
□ Medium Silt - 10mg/ml
• Coarse Silt - 10mg/ml
■ Sand - 200 mg/ml

Fig. 1—Adsorption isotherms—paraquat on Georgia I sediments.

sorbents can be found in the literature (1, 13). Freundlich and Langmuir equations have both been used to describe the isotherms. When applicable, as with the systems used here, the hyperbolic Eq. [1] has the advantage of reducing in both the high concentration and low concentration limits to simpler forms, each depending on a single empirical parameter. In the low concentration limit where $K_pC \ll X_c$, which is the loading range for most environmental applications:

$$X = K_pC \qquad [2]$$

where K_p is a measure of the bonding strength for paraquat.

PARAQUAT DISTRIBUTION IN NATURAL SEDIMENTS

In the natural sediments that were spiked with paraquat and then fractionated by particle-size, paraquat was concentrated heavily in the silt and clay fractions. Paraquat concentration peaked in the coarse to medium clay, whereas paraquat mass peaked in the silt or coarse clay fractions. Concentration peaks were noteworthy because the ratios of concentrations for some of the individual fractions to the mean concentrations commonly reached values of 100 or greater. In the high-sand sediments (Georgia I and II and the Santa Maria River), the coarse clay accounted for 1% or less of the sediment mass, but contained 50 to 60% of the paraquat. In contrast, the low-sand sediment from Macon Bayou had 36% coarse clay that carried 68% of the total sorbed paraquat. The sand fractions contained < 10% of the paraquat in all sediments even though sand made up as much as 99% of the total sediment mass. Overall paraquat distributions were quite similar in all the sediments.

Discernible differences were observed in relative behavior of the different sediments during the particle size separation procedure. The sediments that were relatively low in silt and clay fractionated much more cleanly than those having higher percentages of fines. In sediments having low silt and clay contents, the five washes used in separating the sand and silts yielded clean fractions (that is, the later washes extracted very small amounts of material finer than that being washed). Sediments higher in silt and clay gave less stable fractions that tended to disperse further into finer particles with each successive resuspension. The resulting discarded washes contained noticeable amounts of fine particulates and paraquat; this was reflected in the low apparent paraquat recoveries in the Macon Bayou and Weatherford Lake sediments. This ambiguity in particle size separation also tended to reduce the degree of spiking in paraquat (mass) distribution in the sediments high in silt and clay.

RELATIONSHIP OF PARAQUAT DISTRIBUTION TO PARTITION COEFFICIENTS

In a natural sediment system containing various size fractions, where each fraction competes independently for paraquat,

$$X^i = X_c^i K_p^i C/(X_c^i + K_p^i C) \qquad [3]$$

where i designates the (i)th fraction. Paraquat mass balance dictates that

$$\Sigma_i X^i f^i = \overline{X} \qquad [4]$$

where f^i is the fraction of the total mass represented by component i and $\overline{X}$ is the mean paraquat concentration in the sediment.

Substituting X^i from Eq. [3] into Eq. [4]:

$$\Sigma_i[X_c^i K_p^i C/(X_c^i + K_p^i C)] f^i = \overline{X}. \qquad [5]$$

In the low concentration limit, Eq. [5] becomes

$$\Sigma_i K_p^i C f^i = \overline{K}_p C = \overline{X}$$
$$\text{or } C = \overline{X}/\overline{K}_p \qquad [6]$$

where $\overline{K}_p$ is the mean partition coefficient defined by

$$\overline{K}_p = \Sigma_i K_p^i f^i. \qquad [7]$$

Substituting Eq. [6] into Eq. [3], in the low concentration limit

$$X^i = K_p^i(\overline{X}/\overline{K}_p). \qquad [8]$$

Thus, given the partition coefficients and mass fraction for each size fraction and mean concentration $\overline{X}$, the paraquat distribution can be computed. The K_p^i values in Table 2 were determined on the local (Georgia I)

Table 4—Calculated vs. measured paraquat distribution

Fraction	Paraquat distribution			
	Computed		Measured	
	Conc.	Amount	Conc.	Amount
	ppm	mg	ppm	mg
	Georgia I			
Sand	1	0.8	1	0.8
Coarse silt	33	1.5	21	0.9
Medium silt	46	1.5	52	1.7
Fine silt	330	4.6	330	4.6
Clay	990	14.4	970	14.1
	Georgia II			
Sand	1	1.1	2	2.2
Coarse silt	37	0.5	36	0.5
Medium silt	51	0.9	83	1.4
Fine silt	370	3.3	550	4.8
Clay	1,100	15.6	830	11.7

stream sediment. Calculated paraquat distributions from Eq. [8] compare well with the measured values for local sediments (Table 4).

In lieu of measuring the partition coefficients on all particle size isolates for each sediment, a less ambitious approach was suggested by the similarity in paraquat concentration distribution in all sediments. Even though the actual concentration in a given fraction differed widely from one sediment to another, due mainly to differences in the particle size makeup of the individual sediments, the relative concentration distributions were similar.

Based on the hypothesis that relative paraquat concentrations or relative K_p's of different size fractions (within a given sediment) are constant for all sediments, the set of K_p's determined on local sediments was used to compute the paraquat distributions in nonlocal sediments (Table 5). Given the experimental difficulties associated with the fractionation and subsequent paraquat analyses on these sediments, the computed distributions closely agree with the measured distributions. This agreement does not preclude considerable variations in absolute values of the partition coefficients in different sediments, however.

Table 5—Calculated vs. measured paraquat distribution in nonlocal sediments

	Computed from K_p's	Measured
	ppm	
Santa Maria River		
Sand	3	2
Coarse silt	210	160
Medium silt	290	920
Fine silt	2,100	2,300
Clay	6,300	6,000
Macon Bayou		
Sand	0.04	5
Coarse silt	4	2
Medium silt	4	4
Fine silt	25	9
Clay	76	83
Weatherford Lake		
Sand	0.2	1
Coarse silt	15	7
Medium silt	21	70
Fine silt	150	92
Clay	440	280

Table 6—Paraquat distribution in hectorite clays

Particle size range	Spin time	Total clay	Total paraquat	Paraquat conc.†
μm	min/rpm	mg	μg	ppm
NH_4^+-Hectorite no. 34	$\bar{X}$ = 452 ppm	C_{clay} = 12.27 mg/ml		
2.0 –0.15	5/10,000	138	40	283
0.15 –0.065	25/10,000	112	74	673
0.065–0.044	55/10,000	107	81	743
0.044–0.035	85/10,000	148	93	649
0.035–0.030	115/10,000	132	80	597
0.030–0.026	160/10,000	185	59	270
% recovery clay = 94.1%		% recovery paraquat = 100.3%		
Na^+-Hectorite no. 34	$\bar{X}$ = 428 ppm	C_{clay} = 14.3 mg/ml		
0.2 –0.15	5/10,000	162	53	325
0.15 –0.084	15/10,000	87	52	594
0.084–0.059	30/10,000	75	69	932
0.059–0.042	60/10,000	100	59	593
0.042–0.034	90/10,000	120	61	511
0.034–0.030	120/10,000	125	56	451
0.030–0.027	150/10,000	97	33	344
0.027–0.015	120/20,000	138	26	193
% recovery clay = 99.9%		% recovery paraquat = 103.0%		

† Paraquat concentration relative to dry clay mass.

RELATIONSHIP BETWEEN PARTITIONING AND CEC

The primary sorption mechanism for paraquat on soil materials is through the cation exchange process. Because CEC is an easily measured and widely catalogued property of natural soils and sediments, a relationship with CEC would be a useful tool for predicting sorption characteristics. Therefore, the relationship between CEC and paraquat partitioning was examined.

The paraquat distributions in Table 3 are recorded as percentages of the CEC for each fraction. Although a relationship between the number of charge sites per unit mass of sorbent apparently exists, there are also variations in effectiveness of charge sites on the different fractions for sorbing paraquat. This is shown by the variations in the percent CEC column of Table 3. This trend was observed in all the sediments, but the actual percentages were a function of the degree of paraquat loading relative to the CEC of the whole sediment. These observations are indicative of the presence of "high affinity" charge sites noted in other systems (3, 4, 8, 9, 12) and are analogous to the results for the model clay systems discussed later.

PARAQUAT DISTRIBUTION IN MODEL CLAY SYSTEMS

Results of paraquat partitioning in hectorite clay slurries are given in Table 6. Centrifugation times were selected to give roughly equal clay masses in each size separate. Paraquat concentrations peaked in the size fraction having equivalent Stokes radii in the range of 0.065–0.044 μm in the NH_4^+-hectorite preparation. The peak concentrations are worthy of note because they ranged from two to five times higher than the least active fraction. Similar behavior was observed in standard montmorillonites.

The ammonium-measured CEC showed little or no variation over the hectorite size fractions. Apparently,

as in the natural sediment systems, paraquat sorptive preferences are not simple functions of total charge sites available when paraquat concentrations are much less than the CEC. For situations in which paraquat is not present in sufficient quantity to satisfy all available charge sites, the possibility for preferential partitioning to the high affinity sites becomes important. Weed and Weber (13) reported good correlations of CEC with maximum paraquat adsorption capacity on the expanding three-layer minerals. This result was not found in the present systems when paraquat was present in amounts sufficient to satisfy 10% or less of the CEC. Even though all fractions had nearly equivalent numbers of total sites available, the most strongly adsorbing fractions apparently had a greater proportion of high affinity sites capable of adsorbing small amounts of paraquat on a selective basis. Garcia-Miragaya and Page (3) have explained the preferential adsorption of cadmium ions on montmorillonite in terms of high affinity sites and similar indications have been reported in a variety of other systems (4, 8, 9, 12).

In the pure clay systems, paraquat can be easily monitored by UV light absorption, using blank clay suspensions to cancel background light absorption and scattering caused by the clay. Also, sorbed paraquat can be distinguished from free (solution) paraquat. On a hectorite clay, the sorbed paraquat shows maximum light absorption at 275 nm, whereas free paraquat shows peak absorption at 260–262 nm. In addition, the sorbed paraquat spectral band is much sharper with more vibronic resolution than the solution spectral band.

A hectorite suspension (11.2 mg/ml) was spiked with paraquat at 10,000 ppm (relative to clay mass), and the paraquat band was followed in the suspended phase as a function of spin time at 20,000 rpm. Initially, as expected, the suspension spectrum was that of sorbed paraquat. After spinning 1 hour, about 1% of the paraquat remained in the suspended (water) phase; still the absorption spectrum was totally dominated by sorbed paraquat. The solution phase was followed through 4 hours of centrifuging until the paraquat level dropped below the detection limit of 50 ppb (relative to solution volume). The paraquat absorption spectrum eventually showed free paraquat, but the majority of the paraquat remained in the sorbed form throughout centrifugation.

The point here is that sediment-water phase separations are not absolute. The distinction between sorbed paraquat and solution paraquat is dependent upon the actual phase separation technique, which may not distinguish sorbed from free paraquat. Moreover, paraquat may be sorbed on particulates that are not removed by the phase separation procedure. In most sorbate-sorbent systems, sorption is measured solely by phase separation and subsequent analysis of the isolated phases. It should be emphasized that "solution" phase measurements do not necessarily measure dissolved or "free" compound. This effect may be important when describing the aqueous phase chemistry of compounds that are equilibrated with sediments. This phase-separation effect is much more accentuated in sorbate-sorbent systems where K_p is large (10^3 or greater). If sorption is described by the linear Eq. [2], then the fraction of the compound that is sorbed (F) can be expressed as

$$F = \varrho K_p/(1 + \varrho K_p) \quad [9]$$

where ϱ is the sorbent concentration.

For paraquat, where K_p for clay size particles is of the order of 10^4, sorbent concentrations of 10^{-4} kg/liter or 1 mg/liter will sorb 50% of the paraquat. In the hectorite-paraquat system, the fine particulate sorbent concentration, which remained suspended, was sufficient to sorb the major fraction of paraquat even after 4 hours of spinning at 20,000 rpm. Similar reasoning might also apply to natural sediments.

CONCLUSIONS

The sorption of paraquat on natural sediments can be described by a Langmuir isotherm. The adsorption maxima correspond well with the NH_4^+-measured CEC's. The isotherm coefficient determined on individual particle-size fractions of a natural sediment can be used to compute the paraquat distribution as a function of a particle size in the whole sediment. In terms of paraquat concentration, this distribution is quite similar on all sediments examined. Paraquat concentration peaked in clay or fine silt fractions and generally showed a 20- to 50-fold reduction in the medium and coarse silts and as much as a 1,000-fold reduction in the sand (relative to peak concentrations).

The impact of particle-size preferential adsorption of organic cation species on transport of pollutants along water-courses and in overland flow runoff situations is a factor that will demand attention in future efforts to understand environmental problems. The available sediment control technology in agricultural runoff situations (no-tillage farming, terracing, contours, etc.) is most effective in limiting transport of the heavier sediment-size fractions. These fractions, however, are the least effective carriers of sorbed paraquat. For instance, if one completely abated transport of the sand fraction of the Georgia I sediment, the sediment mass transport would be reduced 89%, but the transported paraquat load would be reduced by only 3%. This point is somewhat exaggerated, however, because most sediment control measures also substantially reduce the runoff water volume available for carrying the fine materials, which are effective carriers of paraquat.

The wide range of sorbed paraquat concentrations from the sand to the silt (Table 3) is indicative of the range of exposure that could be encountered by various organisms in the environment. Similarily, the effective rates of chemical, photochemical, and biological degradation could be substantially affected.

ACKNOWLEDGMENT

The authors thank Mr. Edmond Deluca and Mr. Daniel Thoman for technical assistance.

LITERATURE CITED

1. Burns, G., M. H. B. Hayes, and M. Stacey. 1973. Some physical-chemical interactions of paraquat with soil organic materials and model compounds. Weed Res. 13:79–90.
2. Fields, D. E. 1976. CHNSED: Simulation of sediment and trace contaminant transport with sediment/contaminant interaction. Natl. Sci. Found., Washington, D.C. ORNL/NSF/EATC Rep.

no. 19. Natl. Tech. Inf. Serv., U.S. Dep. of Commerce, Springfield, Va.

3. Garcia-Miragaya, J., and A. L. Page. 1976. Influence of ionic strength and organic complex formation on the sorption of trace amounts of Cd by montmorillonite. Soil Sci. Soc. Am. Proc. 40: 658–663.
4. Haydson, J. F. 1960. Co reaction with montmorillonite. Soil Sci. Soc. Am. Proc. 24:165–168.
5. Jackson, M. L. 1956. Soil chemical analysis-Advanced course. University of Wisconsin Press, Madison, Wis.
6. Johnson, R. C., and N. H. Crawford. 1976. Development of watershed erosion and sediment transport model. Hydrocomp Inc., Palo Alto, Calif. Prepared for USEPA, Athens, Ga. Inerim Rep. under Contract no. R803726-01. EPA, ORD Report, Contract no. R803726-01, Hydrocomp Inc., Palo Alto, Calif.
7. Knott, G. 1975. MLAB an on-line modeling laboratory. 5th Ed. Div. Computer Res. and Technol., Natl. Inst. of Health, Bethesda, Md.
8. McLaren, R. G., and D. V. Crawford. 1973. Studies in soil copper: II. The specific adsorption of Cu by soils. J. Soil Sci. 24(4): 443–452.
9. Nelson, J. L., and S. W. Melsted. 1955. The chemistry of zinc added to soils and clays. Soil Sci. Soc. Am. Proc. 19:439–443.
10. Pope, J. D., Jr., and J. Benner. 1974. Colorimetric determination of paraquat residues in soil and water. J. Assoc. Off. Anal. Chem. 57(1):202–204.
11. Shen, H. W. 1976. Sediment transport models. Chap. 26. p. 1–33. *In* H. W. Shen (ed.) Stochastic approaches to water resources. H. W. Shen, P. O. Box 606, Fort Collins, Colo.
12. Tiller, K. G., and J. F. Hodgson. 1962. The specific sorption of cobalt and zinc by layer silicates. Clays Clay Miner. 9:393–403.
13. Weed, S. B., and J. B. Weber. 1969. The effect of cation exchange capacity on the retention of diquat and paraquat by three-layer type clay minerals: I. Adsorption and release. Soil Sci. Soc. Am. Proc. 33:379–382.